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THE EFFECT OF PARTICLE SIZE ON THE CARRIER-DISTILLATION ANALYSIS OF PuO_2

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by

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The spectrochemical analysis of plutonium metal at Los Alamos Scientific Laboratory involves converting the metal to PuO_2 as shown in the

1 first slide. The PuO_2 is then ground in a mortar. A mixture of Ga_2O_3 and Co_3O_4, the Carrier and Internal Standard (CIS) respectively, is added to the PuO_2 sample. This combination is placed in a plastic vial and shaken using a mechanical mixer. One hundred mg portions of the sample are placed in electrodes and arced. The spectra are recorded photographically and the impurity contents are determined.

Prior to 1960, the PuO_2 and the CIS mixture were ground in a mortar. In 1960, James H. Muntz[1] showed that mechanical mixing in a Wig-L-Bug mixer could be substituted for the mortar grinding of the PuO_2 and the CIS mixture (step 4 on slide). This substitution reduced the amount of time and work needed to prepare a sample. Muntz noted during his work that the initial grinding of the plutonium oxide in a mortar was important in obtaining accurate answers when using the plastic vials and the mechanical mixer.

This current study was undertaken to determine the effect of particle size on the carrier-distillation analysis of PuO_2 and to explain how to avoid the difficulties caused by large PuO_2 particles.

2 The next slide is a scanning electron photo micrograph of several large PuO_2 particles. The micrograph is at 500X. Note the cave-like opening in the center particle. These particles are in the range of 75 to 150

3 micrometers in size. The next slide is a scanning electron photo micrograph of the CIS mixture. It is also at 500X. The smallest particles shown are approximately 1 micrometer in size and the largest particles are approximately 10 micrometers in size.

For this work, 15 g of PuO_2 were prepared by igniting chunks of plutonium metal. The entire 15 g of PuO_2 was mixed and ground in a mortar. A 5 g portion (labelled P_1) was removed and the remaining 10 g of PuO_2 was ground further. A second 5 g portion of PuO_2 (P_2) was removed and the remaining 5 g of PuO_2 underwent further grinding. This third portion was labelled P_3.

The impurity content of the three designated portions should be identical because they originated from the same source metal and were homogenized by grinding in a mortar prior to being separated into P_1, P_2, and P_3.

Portions of the source plutonium metal, other than the 15 g of PuO_2 used in this study, were analyzed repeatedly and the impurity content was well characterized. Cobalt was not detected at less than 2 ppm.

4 The next slide presents the particle size distribution for each of the 3 samples and for a standard. The separation into these particle size ranges was made using sieves with screen sizes of 150, 75, and 45 micrometers.

The sieved PuO_2 was analyzed in two ways. First, each particle size range was analyzed then P_1, P_2, and P_3 with their combination of particle sizes were analyzed.

5 The next slide shows the relative intensity of five elements for the various particle sizes. The first observation to note is that the relative intensity of the five elements increases as the particle size of the PuO_2 becomes smaller. The particle size of the cobalt is approximately 10 micometers and it is not ground with the PuO_2 but only mixed using the mechanical mixer.

The use of visual comparison of impurity line intensity to determine impurity concentration, when the sample is composed of large particles of PuO_2 and the standards are made up of small particles would result in an estimate of impurity content that would be significantly lower than it actually was.

6 The next slide presents the percent increase of intensity for the five elements from the largest PuO_2 particle size to the smallest particle size .

7 The next slide shows the relative intensity for the same five elements obtained by analyzing P_1, P_2, and P_3. P_1 is composed of 20% large particles (75 to 150 μm), 46% medium particles (45 to 75 μm), and 34% small particles (< 45 μm).

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P_2 has 39% medium and 61% small particles while P_3 is composed of particles all smaller than 45 micrometers. Again note the intensity increase of cobalt from P_1 to P_3 even though its particle size does not change.

8 The next slide shows tne percent increase of intensity for the five elements from P_1 to P_3. When intensity ratios versus concentration (e.g. I_{Fe}/I_{Co} versus ppm) are used to determine tne concentration of impurities, the greatest change in concentration from P_1 to P_3 will be for iron because the intensity of iron increased significantly less than that for cobalt from P_1 to P_3.

9 Tnis is snown on the next slide. Tne concentration of iron shown for P_1 (which contains large PuO_2 particles) is significantly higher than the correct value. Note the plateau at P_2 and P_3 for all the elements.

10 Tne next slide gives the analytical results found for the source PuO_2 used in this study. The spectrographic results are from laboratories other than Los Alamos. Tne values obtained for P_2 and P_3 agree with the independently determined values.

1 The next slide deals with the explanation of why the intensity of cobalt increases with decreasing PuO_2 particle size. Tne particle size of the CIS mixture is in the approximate range of one to ten micrometers. Tne Wig-L-Bug mechanical mixer does a fine mixing job but does little grinding of the refractory PuO_2 particles.

The explanation offered is that the smaller cobalt particles are entrapped in the cracks and fractures present in some of the much larger PuO_2 particles, especially when there is present a mechanism for causing the entrapment.

Tnis slide shows the relative intensity of cobalt under a number of circumstances. Part A deals with the grinding in a mortar of coarse PuO_2 with CIS mixture. At zero seconds of grinding, the intensity of cobalt is higher than it is after 25 seconds of grinding. Tne intensity of cobalt increases with more than 25 seconds of grinding.

There are two things happening during the grinding process. In the first 25 seconds of grinding the large PuO_2 are being fractured but more importantly the cobalt is being entrapped by these large fractured PuO_2 particles with the grinding action of the pestle being the mechanism for accomplishing this. In the latter stages of grinding, the large and possibly fractured PuO_2 are completely broken apart freeing both the impurities and the entrapped cobalt to produce greater line intensity for both.

In part B of the slide, coarse and fine PuO_2 are mixed with CIS in a plastic vial containing two beads. A mechanical mixer is used to shake the vials for 30 seconds. The intensity of cobalt from the coarse PuO_2 sample is much less than that from fine PuO_2. The mechanism for the entrapment of cobalt is the large PuO_2 particles as well as the two beads.

In part C, coarse and fine PuO_2 are shaken in a vial without two beads. The intensity of cobalt from the coarse PuO_2 sample is less than that from fine PuO_2 although the difference is not as dramatic as in part B. The mechanism here is the large PuO_2 particles bumping together during the shaking.

The data shown in this slide indicate that the principal factor causing the lower relative intensity for cobalt, using plastic vials, beads, and the Wig-L-Bug mechanical mixer, is the entrapping of cobalt by the large and irregular-shaped PuO_2 particles.

The presence of large particles of PuO_2 depends on the size and shape of the plutonium metal sample before ignition. Waterbury[2] et al studied the ignition of plutonium metal and found that lathe turnings burned more quickly and more completely than chunks at a given temperature. We observed that turnings produce a finely powdered oxide while chunks of plutonium produce many large abrasive particles. This PuO_2 must be thoroughly ground in a mortar to reduce all particles to less than 45 micrometers.

The next few slides are scanning electron photomicrographs of the various sizes of particles studied in this work. Jim Lehmann, CMB-11, did all the scanning electron microscope (SEM) work reported on here.

The first of these SEM slides shows PuO_2 particles in the 75 to 150 micrometer range. All of these SEM slides are at 200X magnification. Note

the cracks and fractures in the particle in the center of the slide. This is an example of a PuO_2 particle that could entrap relatively large amounts of the internal standard, cobalt. It was also observed that greater variability was obtained when working with coarse PuO_2 of this size than from finely ground PuO_2. This variability may be due to the varying quantities of particle sizes present in a coarse sample as well as sampling variance due to the large particles as discussed by Harris and Kratochvil.[3]

13 The next slide shows PuO_2 particles in the 45 to 75 micrometer range.

14 The next slide presents PuO_2 particles that are less than 45 micrometers in size. It is this size that is recommended for accurate analysis.

15 The last slide shows the CIS mixture that contains the internal standard, cobalt. These particles range from approximately 1 μm to 10 μm in size. I believe it is apparent that these small particles could become entrapped in the much larger PuO_2 particles.

In conclusion, we have shown how the relative intensity of the impurity elements increases with decreasing PuO_2 particle size. Further, the line intensity of the added internal standard, cobalt, also increases with decreasing PuO_2 particle size. Accurate spectrochemical results are obtained when the PuO_2 particle size has been reduced to 45 micrometers or less.

A particle size of 45 micrometers or less can be obtained for the PuO_2 sample by 60 seconds of vigorous grinding in a mortar per each 100 mg of PuO_2. The analyst should check the particle size, at least once, by passing the ground PuO_2 through a No. 325 mesh screen. A mechanical mixer can then be used for further preparation of the PuO_2 sample.

I wish to thank all of the people in the spectrochemical section, especially D. W. Steinhaus, for their help. And I wish to thank CMB-1 Group Leader, G. R. Waterbury for his assistance in preparing this report. Jim Lehmann, CMB-11, did the scanning electron microscope work in the PuO_2 and CIS particles.

References

1. J. H. Muntz, Los Alamos Scientific Laboratory, unpublished data, 1960.

2. G. R. Waterbury, R. M. Douglass, and C. F. Metz, "Thermogravimetric Behavior of Plutonium Metal, Nitrate, Sulfate, and Oxalate," Anal. Chem. 33, 1018 (1961).

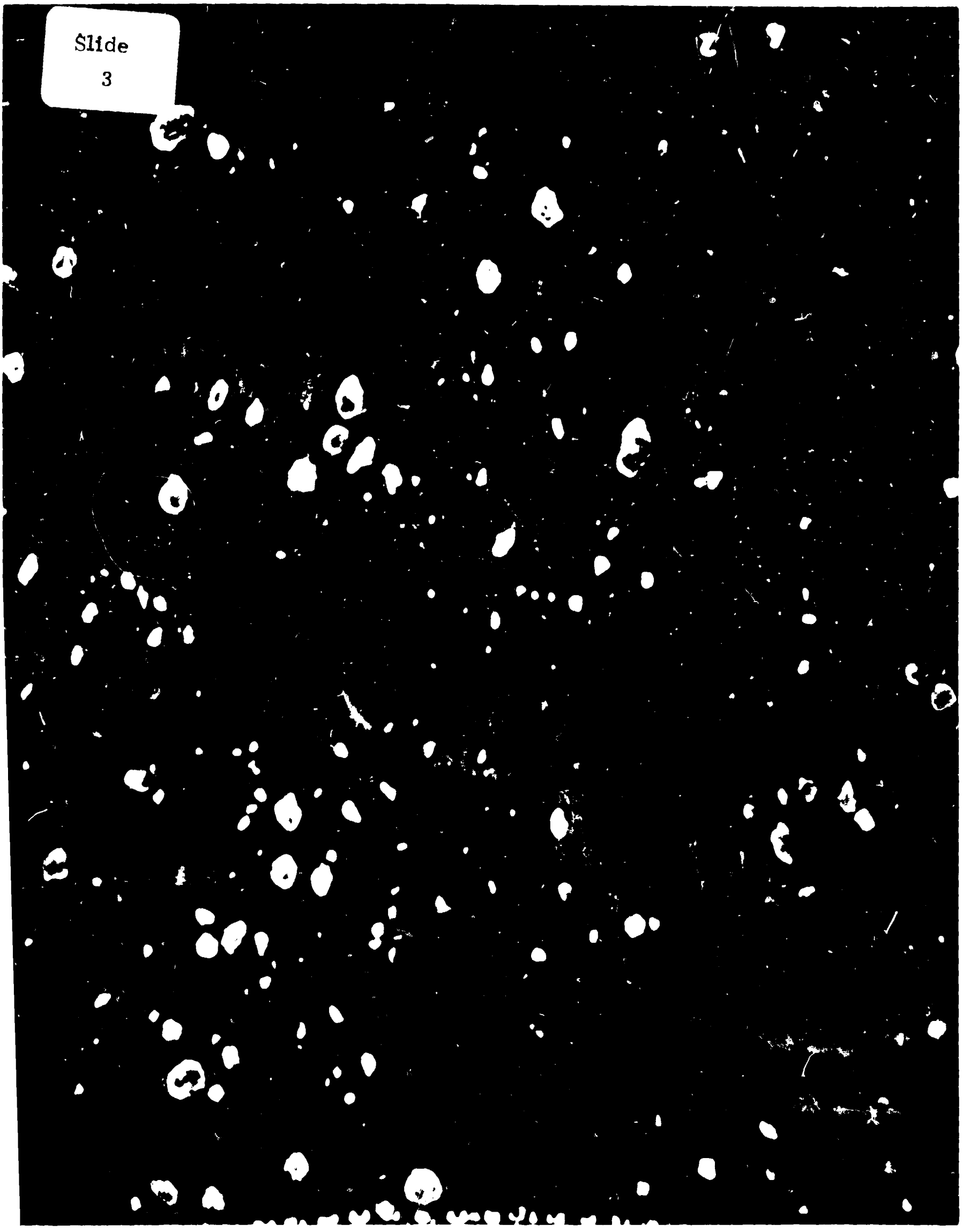
3. W. E. Harris, and Byron Kratochvil, "Sampling Variance in Analysis for Trace Components in Solids," Anal. Chem. 46, 313 (1974).

Slide
1

SPECTROCHEMICAL ANALYSIS OF PLUTONIUM METALS

1. $Pu + O_2 \longrightarrow PuO_2$
2. PuO_2 is ground in mortar
3. $Ga_2O_3 + Co_3O_4$ (CIS) added
4. PuO_2 + CIS mixed in plastic vials
5. Electrode samples are arced
6. Spectra are recorded photographically
7. Concentrations of impurities are determined


Slide
2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3

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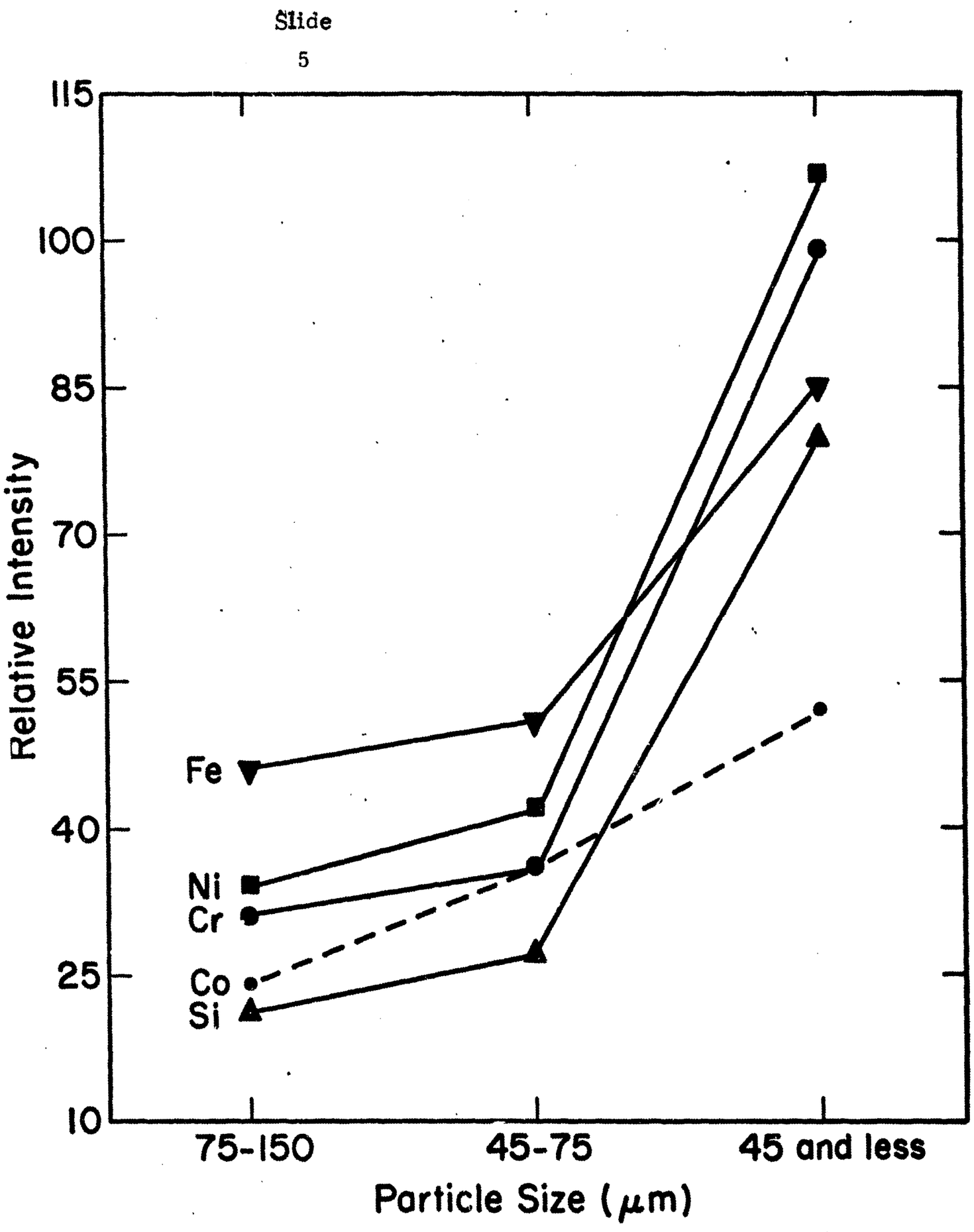
4

PARTICLE SIZE DISTRIBUTION FOR P_1, P_2, and P_3 AND STANDARD PARTICLE SIZE

	150 to 75 μm(%)	75 to 45 μm(%)	Smaller than 45 μm(%)
P_1	20	46	34
P_2	0	39	61
P_3	0	0	100
Standard	0	0	100

Slide
5


115
100
85
70
55
40
25
10
Relative Intensity
Fe
Ni
Cr
Co
Si
75-150
45-75
45 and less
Particle Size (μm)

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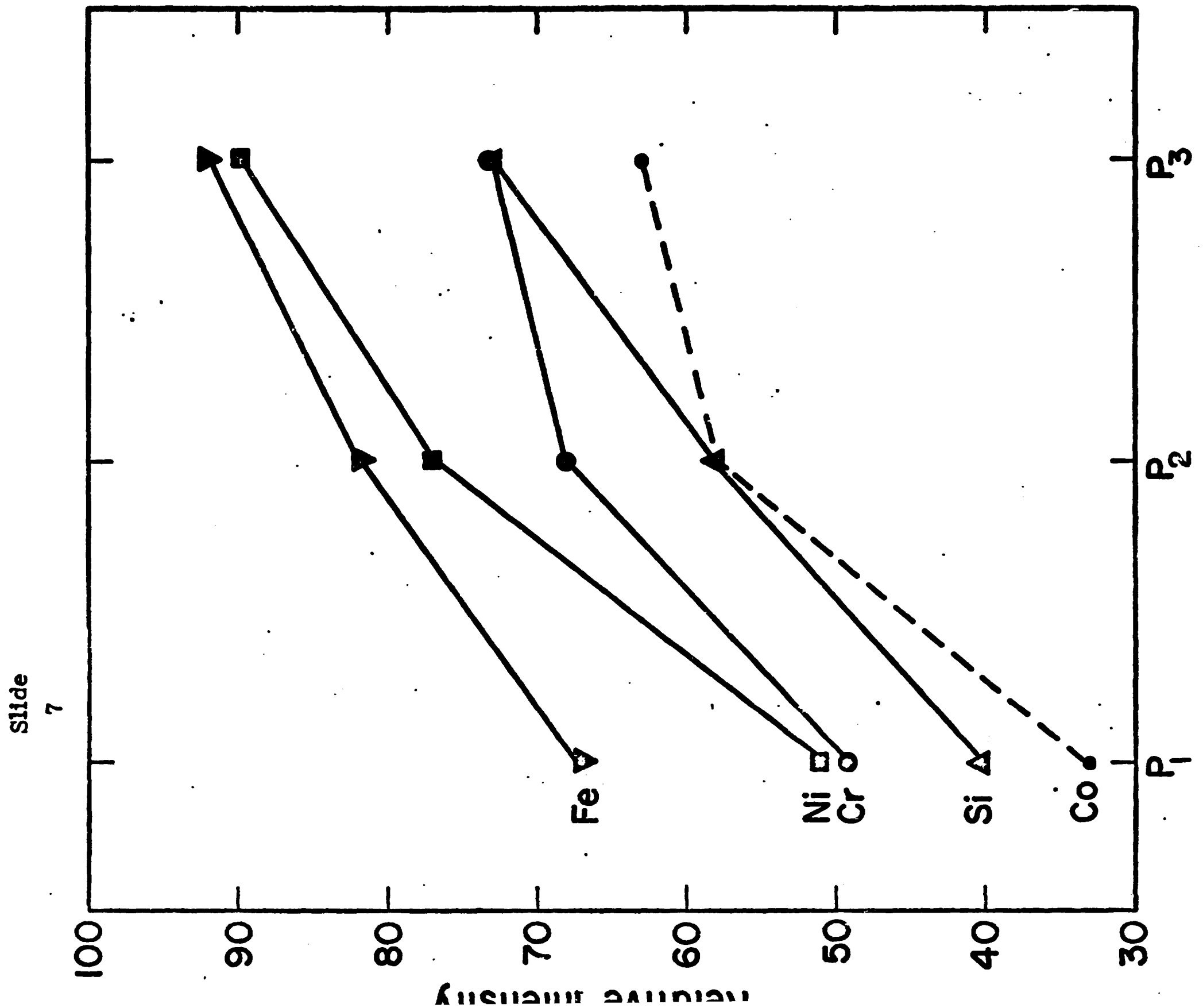
INCREASE IN INTENSITY FOR ELEMENTS FROM LARGEST TO SMALLEST PuO_2 PARTICLE SIZE

Element	Increase in Intensity (%)
Fe	85
Cr	210
Ni	215
Si	280
Co[a]	117

[a] Internal Standard


Slide 7
Relative Intensity
100
90
80
70
60
50
40
30
P_3
P_2
P_1
Fe
Ni
Cr
Si
Co

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8

INCREASE IN RELATIVE INTENSITY FOR IMPURITY ELEMENTS FROM P_1 to P_3

Element	Intensity		Increase
	P_1	P_3	%
Fe	67	92	37
Cr	49	73	49
Ni	51	90	76
Si	40	73	80
Co	33	63	91

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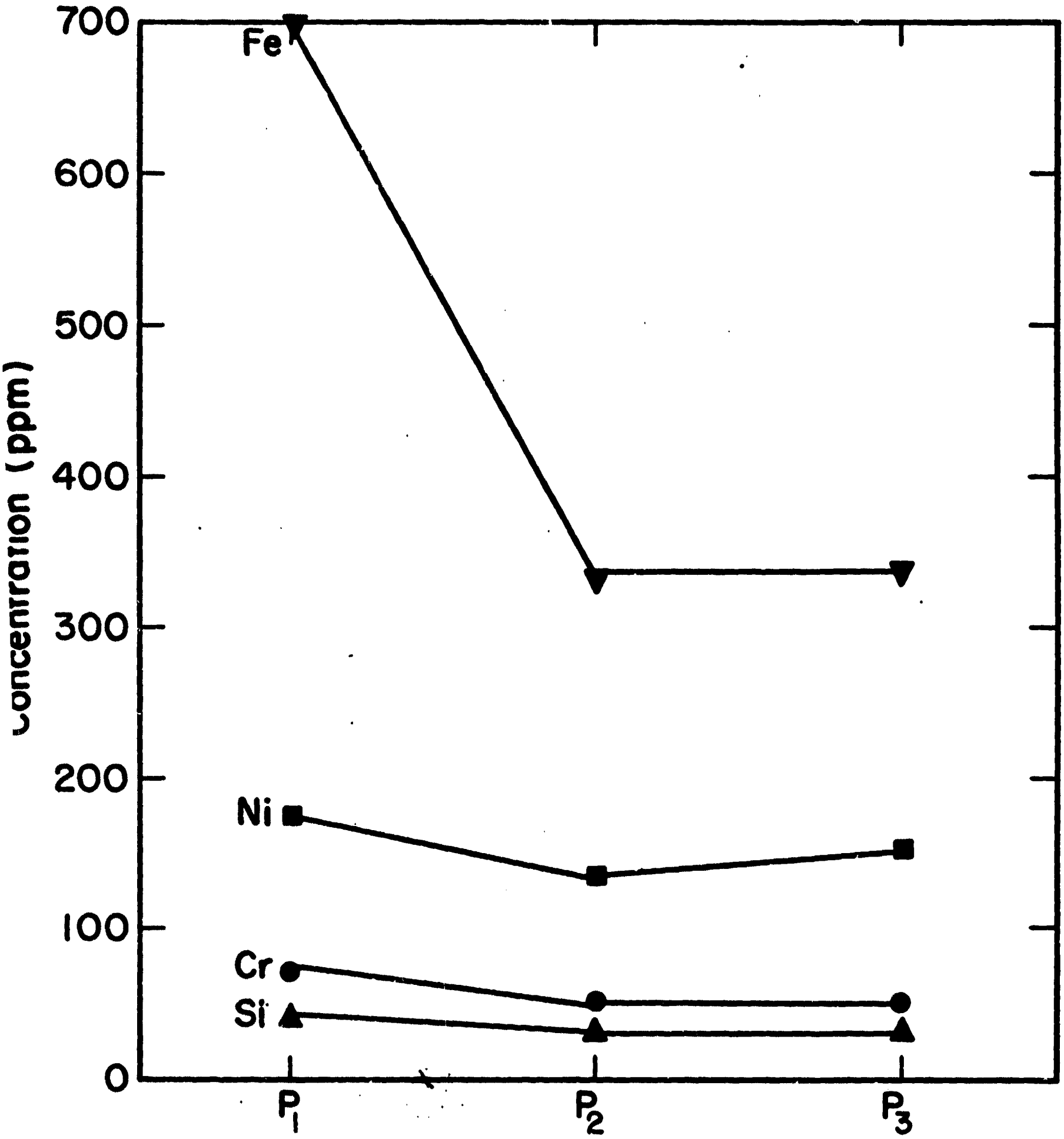
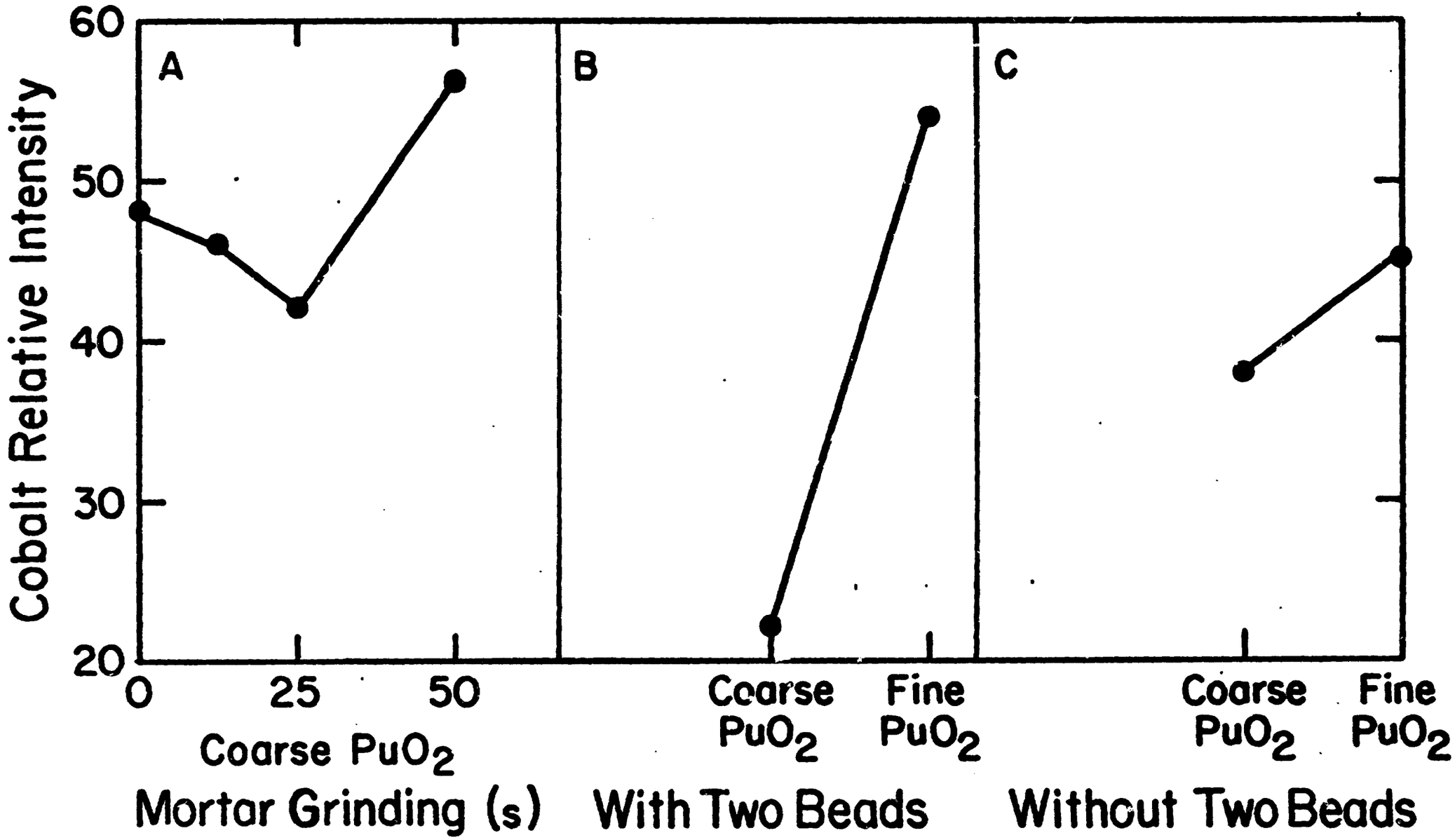

700
600
500
400
300
200
100
0
Concentration (ppm)
Fe
Ni
Cr
Si
P1
P2
P3

Slide
10

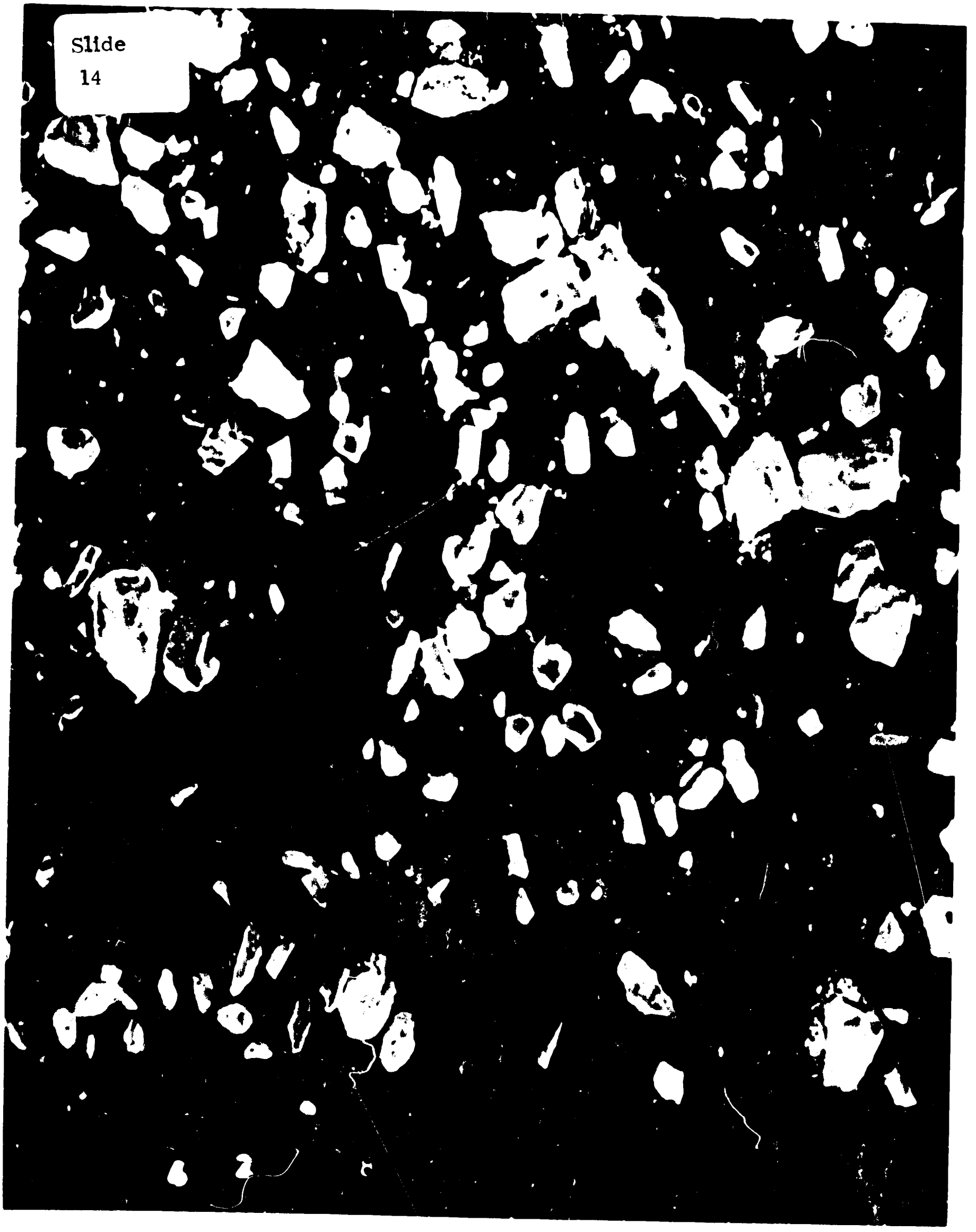
COMPILATION OF ANALYTICAL RESULTS ON PuO_2 STUDIED

Element	Average Concentration, ppm			
	Atomic Absorption	Spectrographic	Chemical	P_2 and P_3
Fe	345	345	350	340
Si	-	30	-	30
Ni	123	135	-	140
Cr	45	45	-	50


Cobalt Relative Intensity
60
50
40
30
20
A
B
C
0
25
50
Coarse PuO2
Coarse PuO2
Fine PuO2
Coarse PuO2
Fine PuO2
Mortar Grinding (s)
With Two Beads
Without Two Beads


Slide
12


Slide
13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